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Vibrational analysis of *L*-proline

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Abstract : Using Wilson's FG matrix method, a normal coordinate analysis of the spectral frequencies and the assignments of the Fourier transform infrared and Raman spectrum of *L*-proline are performed here The vibrational frequencies and the potential energy distributions of the 22 in-plane and 14 out-of-plane vibrations are presented and the evaluated vibrational frequencies are compared with the experimental values

Keywords : Infrared and laser Raman spectrometry, normal coordinate analysis, *L*-proline

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1. Introduction

The investigations on the vibrational spectra of 2-pyrrolidinone and related compounds (γ-butyrolactone) reported earlier [1–4] are of interest due to their biological importance and structural similarity to cyclic peptides. Apart from this, compounds like *L*-proline is also of special significance as they find applications in microbiological test (culture media), biochemical and nutritional research. But still, a complete study on the vibrational spectra of *L*-proline is the lacuna at present. This necessitates the need to obtain more reliable assignments for these molecules of high chemical value.

2. Experimental

L-proline was obtained commercially from Reidel deHaen Switzerland, and it has been used as such. A Shimadzu 8101 Spectrometer was used to record the FTIR spectrum from 4000–400 cm^{-1}. The Raman spectrum was measured on Dilor Z24 Raman Spectrometer equipped with a Spectra Physics Model 165 argon ion laser operating at 200 mw power on the 488 nm line. The bands obtained are correct to within ± 1 cm^{-1}.

3. Normal-coordinate calculation

Although, some previous spectroscopic work and vibrational calculations were reported on proline and their derivatives, they either lacked Raman studies, or were incomplete of the infrared region. The purpose of this work is to characterise more completely the vibrational motions of the *L*-proline. The structural parameters employed in this work were transferred from the McDermott [2], Peek and McDermott [3] and other related molecules (they are bond distances C^1–N = 1.404, C^1–C^2 = 1.532, C^2–C^3 = 1.545, C^3–C^4 = 1.550, C^4–N = 1.456, C–H = 1.079, N–H = 1.020 in angstroms and angles NCC = 107.8, CCC = 105.7, CCC = 106.9, NCC = 108.2, CNC = 114.7, CNH = 120.9 in degrees). The normal modes of vibrations are determined using the method of Wilson *et al* [5]. The structural assumptions suggest *L*-proline to be of C_1 structure. For a C_s structure, by assuming COOH as a point mass, there are 36 normal modes of vibrations which can be distributed as 22 a' (in-plane) and 14 a'' (out-of-plane) vibrations and all are Raman and infrared active.

The conformation adopted for the normal coordinate analysis is shown in Figure 1. The stretching and some bending internal coordinates are also depicted in that figure. The

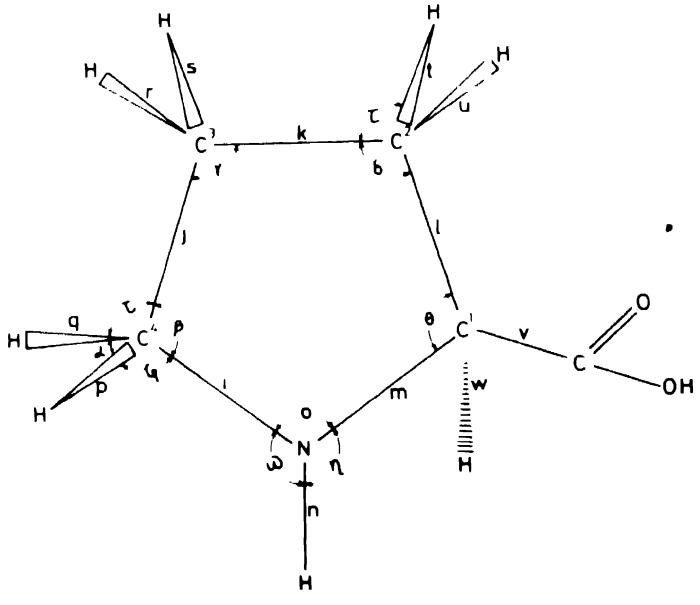

Figure 1. Molecular model and internal coordinates for *L*-proline.

simple UBFF model generally ignores the interaction between non-neighboring stretching vibrations and between bending vibrations. So, the average deviation between the calculated and the observed frequency is usually large. To obtain a fair agreement between the calculated and the observed frequencies, the modified UBFF has been used for this analysis. This type of field contains a simple Urey-Bradley-Shimanouchi force field for in-plane vibrations and a valence and valence interaction force function for out-of-plane vibrations. The initial set of force field used for this calculation was transferred from

research reports of McDermott and coworkers [2,3]. A zero-order calculation was carried out with the transferred force constants. The results showed that except for deformational and torsional modes, the calculated values were in good agreement with the experimental values. Hence, the force field was refined by a damped least square technique until a satisfying agreement is established between the experimental and calculated frequencies.

4. Results and discussion

The FTIR and Raman spectra of *L*-proline are shown in Figures 2 and 3. The appropriate final set of force constants used for the normal coordinate calculation is presented in

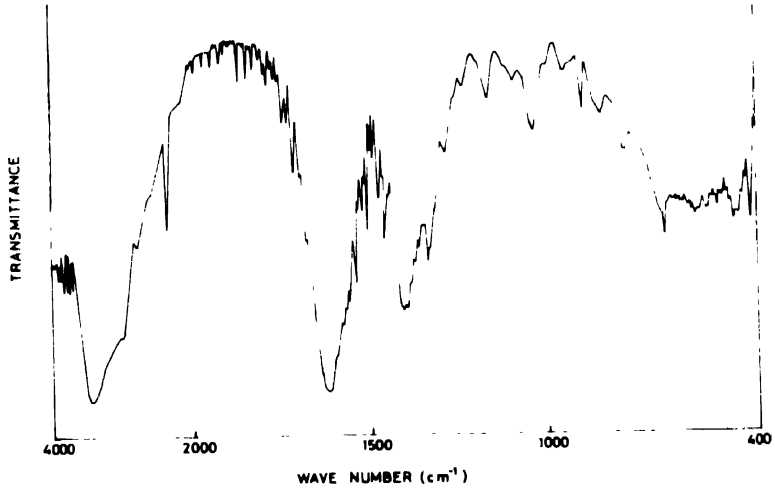

Figure 2. Fourier transform infrared spectrum of *L*-proline

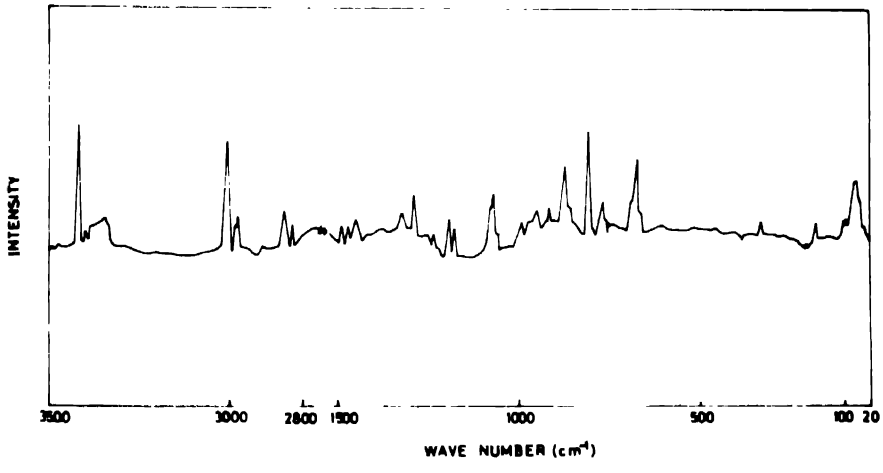

Figure 3. Laser Raman spectrum of *L*-proline.

Table 1. The observed and calculated frequencies are given in Table 2 along with the potential energy distribution. The vibrational assignments for the in-plane and out-of-plane

vibrations are made by referring to the corresponding bands of the related systems and potential energy distributions.

Table 1. Force constants[a] of *L*-proline

Type of constants		Parameters	coordinates involved	Initial value	Final value
		Urey Bradley force constants			
Diagonal constants	stretching	f_i	NC	3 716	3 805
		f_j	CC	2 200	2.215
		f_l	CC^1	3.025	3 176
		f_m	C^1N	6 420	6 486
		f_n	NH	5 681	5 982
		f_p	CH	4 650	4 721
		f_v	$C^1C(OOH)$	2 026	2.026
	repulsion	f_{ri}	NC	0 606	0 452
		f_{rj}	CC	0.450	0 510
		f_{rl}	CC^1	0 450	0 487
		f_{rp}	CH	0 046	0.024
	bending	f_α	HCH	0 510	0 551
		f_β	NCC	0 700	0 726
		f_γ	CCC	0 700	0.494
		f_δ	CCC^1	0 750	0,521
		f_θ	CC^1N	0 786	0 508
		f_ϕ	C^1NC	0.750	0.604
		f_ω	HNC	0 455	0 386
		f_η	HNC^1	0.460	0 295
		f_ξ	HCN	0 690	0 312
		f_τ	HCC	0.690	0 287
		Valence force constants			
Interaction	stretch-bend	$f_{i\xi}$	CN HCN	0 450	0 215
		$f_{j\tau}$	CC HCC	0 300	0 193
	bend-bend	$f_{\omega\xi}$	HNC HCN	0.100	0 086
		$f_{\beta\tau}$	NCC HCC	–0.120	–0 210
		$f_{\theta\tau}$	CC^1N HCC	–0.120	0 008
		$f_{\gamma\tau}$	CCC HCC	–0 120	0.156
	Out-of-plane wagging	f_{on}	NH	0.280	0.111
		f_{ov}	CH	0 325	0.265

Table 1. *(Cont'd.)*

Type of constants	Parameters		coordinates involved	Initial value	Final value
	torsion	$f_{\tau 1}$	NC^1CC	0.250	0.172
		$f_{\tau 2}$	$CCCC^1$	0.120	0.185
		$f_{\tau 3}$	CCCN	0 120	0 091
		$f_{\tau 4}$	$CCNC^1$	0.250	0.105
		$f_{\tau 5}$	CNC^1C	0.300	0.144
	out-of-plane torsion	$f_{on\tau 1}$	NH NC^1CC	0.025	–0.009
	torsion-torsion	$f_{\tau 1\,\tau 2}$	NC^1CC $CCCC^1$	0.050	0.014

[a]Stretching, bending and repulsion force constants are in units of mdyne A^{-1}, internal torsion and valence constants are mdyne A rad^{-2}

Table 2. Calculated and observed frequencies (cm^{-1}) and potential energy distributions of *L*-proline

Calculated frequency	Observed FTIR		Raman frequency		Assignment and PED %	
			In-plane vibrations			
3458	3418	sh	3415	m	ν	(N–H), 94
2986	2975	m	2983	w	ν_a	(C–H) in CH_2, 85
2977	2975	m	2983	w	ν_a	(C–H) in CH_2, 84
2970	2975	m	2983	w	ν_a	(C–H) in CH_2, 84
2851	2861	s	2863	w	ν_s	(C–H) in CH_2, 88
2845	2861	s	2863	w	ν_s	(C–H) in CH_2, 82
2840	2831	w	2832	w	ν_s	(C–H) in CH_2, 89
1522	1508	m	1494	w	ν	(C^1–N), 85, π (N–H), 12
1464	1483	m	1486	w	Sci	(CH_2), 71; t (CH_2), 16
1461	1473	m	1479	w	Sci	(CH_2), 67, t (CH_2), 19
1449	1458	m	1456	w	Sci	(CH_2), 69; ν_a (CH_2)
1347	1340	w	1340	vw	π	(N–H), 78
1292	1305	w	1310	vw	ω	(CH_2), 76, Sci (CH_2), 16
1281	1298	w	1292	w	ω	(CH_2), 78
1271	1290	w	1284	vw	ω	(CH_2), 79
1154	1165	m	1170	vw	ν	(C–C), 65; ν (C–N), 18
1022	1034	m			ν	(C–N), 54; π (N–H), 17
899	895	s	898	m	ν	(C–C), 57
822	810	m	810	m	ν	(C–C), 64; ν (C–N^1), 11
673	689	m	686	m	ν	C^1–C(OOH), 67
660	665	m				ring angle bend, 42
320			328	w	π	C–C(OOH), 44; ν (C–COOH), 16

Table 2. *(Cont'd)*

Calculated frequency	Observed frequency FTIR		Raman		Assignment and PED %
			Out-of-plane vibrations		
2981	2996	w	3003 m	ν	C–H, 79; χ C–H, 14
1211	1235	vw	1230 vw	t	(CH_2), 68
1209	1220	vw	1221 vw	t	(CH_2), 65
1191	1200	vw	1198 vw	t	(CH_2), 58
1061	1070	w	1076 w	χ	(C–H), 61
995	997	w	982 w	γ	(CH_2), 67
931	940	w	951 w	γ	(CH_2), 59
910	920	w	919 w	γ	(CH_2), 67
764	775	w, sh	777 w	χ	(N–H), 68
204			216 w	χ	(C–COOH), 50
198			205 vw		ring twist,
					55 χ (N–H), 27,
				χ	(C–H), 28
169			180 w		ring pucker
					(NC^1CC torsion, 68)
88			84 w		ring twist, 62;
					χ(C–H), 29
66			66 vw		ring twist, 44, χ(N–H), 34
			Group vibrations		
			3275 w	ν	(O–H)
	1620	sh	1640 m	ν	(C=O)
	1440	vw	1449 vw	π	(O–H)
	880	sh	844 w	χ	(O–H)
	545	w	540 w	π	(C=O)
	472	m	476 vw	χ	C–O

Abbreviations used s-strong, m-medium, vw-very weak, sh-shoulder; ν_a-asym. stretching, ν_s-sym. stretching, Sci-scissoring, π-in-plane bending; χ-out-of-plane bending, ω-wagging; γ-rocking and t twisting

Methylene group vibrations :

The methylene group vibrations are assigned on the basis of the spectral similarities to the related five membered ring structures, Raman and infrared frequencies and potential energy distribution. The C–H symmetric stretching vibrations in *L*-proline are attributed to the group of bands in the range 2800–3000 cm^{-1} which is in agreement with the assignment of methylene stretching in the related structure of the molecule reported by McDermott [2] and Satyanarayana *et al* [6]. The potential energy distribution obtained in this analysis shows that the stretching vibrations arising from methylene groups are almost pure.

According to the results of normal coordinate analysis of *L*-proline, the three CH_2 scissoring modes are calculated at 1464, 1461 and 1449 cm^{-1} which coincide with the observed values at 1483, 1473 and 1458 cm^{-1} medium intensity infrared bands. The CH_2 wagging and twisting vibrations generate very weak intensity bands at 1275–1310 cm^{-1}. The potential energy distribution shows that these modes are mixing considerably with other vibrational modes. The weak intensity Raman bands observed at 982, 951 and 919 cm^{-1} have been assigned to CH_2 rocking vibrations.

The medium intensity Raman band at 3003 cm^{-1} and its infrared counterpart at 2996 cm^{-1} have been assigned to C–H stretching mode. The out-of-plane C–H bending vibration in the related five membered ring systems are usually expected in the region near 1100 cm^{-1} [7]. Hence, the weak intensity Raman band observed at 1076 cm^{-1} has been assigned to this mode.

Ring vibrational modes :

The C–C stretching modes are assigned to the infrared bands observed at 1165, 895 and 810 by analogy with the earlier work of Peek and McDermott [3]. The in-plane ring deformational mode in five membered N-heterocyclic molecules are assigned based on the position and intensity of the spectrum and are generally observed around 660 cm^{-1}. Here, this mode is assigned to the medium intensity infrared band at 665 cm^{-1}.

Proceeding towards the lower frequency modes, the weak intensity Raman bands observed at 66, 84 and 205 cm^{-1} have been assigned to the ring twisting modes. The potential energy distribution shows that the N–H and C–H deformational modes have a significant contribution to these modes. The normal coordinate analysis on *L*-proline suggests that the calculated frequency at 169 cm^{-1} is due to the ring puckering mode, which agrees well with the experimental value of 180 cm^{-1}.

The high energy internal modes of vibration of the *L*-proline arise from N–H bond stretch. The medium intensity Raman band observed at 3415 cm^{-1} in *L*-proline has been undoubtedly assigned to N–H stretching mode and this assignment is well supported by the results reported for other related five membered heterocyclic molecules. From the potential energy distribution, it is clear that this mode is dominated by a single vibrational mode.

Considerable disagreement exists amongst those previous work on five membered heterocyclic ring system regarding the in-plane deformational modes of N–H. The broad and moderate intensity absorption is usually the characteristic of out-of-plane N–H deformational mode. This mode is very sensitive to molecular environment and in most of the five membered N-heterocyclic ring system, this mode is Raman inactive. The normal coordinate analysis on *L*-proline suggests that the calculated frequencies at 1347 and 764 cm^{-1} corresponding to the observed infrared frequencies at 1340 and 775 cm^{-1} are due to the in-plane and out-of-plane N–H bending modes.

C–N *vibrations :*

The medium intensity infrared band observed at 1508 cm^{-1} and its weak Raman counterpart at 1494 cm^{-1} has been assigned to C^1N stretching mode. The potential energy distribution obtained in this analysis predicts that this mode is predominantly due to C^1–N stretch coupled with N–H bending. It is higher than that found in 2-pyrrolidinone [2] around 1490 cm^{-1}, and other related five membered ring structures. The C–N stretching vibration has been assigned to the medium intensity infrared band observed at 1034 cm^{-1} which has no Raman counterpart.

COOH *group vibrations :*

The C=O stretching is a characteristic frequency of carboxylic group. The medium intensity Raman band at 1640 cm^{-1} and its broader infrared counterpart observed at 1620 cm^{-1} is assigned to C=O stretching vibrations. The band observed at 3275 cm^{-1} has its origin from the O–H stretching origin. The infrared band at 1440 and 880 cm^{-1} have been assigned to O–H in-plane and out-of-plane bending vibration. The C=O in-plane and out-of-plane bending vibrations are assigned to 540 and 476 cm^{-1} infrared bands and this assignment is made in analogy with the related carboxylic group [8].

All the 36 normal vibrations of *L*-proline are identified and are reasonably assigned with the help of potential energy distribution obtained through normal coordinate analysis. Most of the vibrational assignments presented in Table 2 are in close agreement with those of molecules of related structures. The final set of force constants derived in this analysis are able to provide a good fit between the observed and calculated frequencies.

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References

[1] M J French *Chemical Society, Specialist Periodical Reports, Mol. Spectrosc* **1** 279 (1973)

[2] D P McDermott *J. Phys. Chem.* **90** 2569 (1986)

[3] P S Peek and D P McDermott *Spectrochim Acta* **44A** 371 (1988)

[4] M R Udupa, G Krishnan and Arayamudhan *Inorg Nucl Chem Letts.* **9** 491 (1972)

[5] E B Wilson, J C Decius and P Cross *Molecular Vibrations* (New York . McGraw Hill) (1955)

[6] D N Satyanarayana, S V Kasmir Raja and R Shanmugam *Spectrochim Acta* **43** 501 (1987)

[7] F A Devillanova, K R Gayatri Devi, D N Satyanarayana and Gaetano Verani *Spectrochim. Acta* **35** 1083 (1979)

[8] S Ahmad, S Mathur and P K Verma *Indian J Pure Appl. Phys* **30** 764 (1992)